

METHOD OF MANUFACTURE OF AN ANODE COMPOSITION FOR USE IN A RECHARGEABLE ELECTROCHEMICAL CELL

FIELD OF THE INVENTION

This invention relates to a method of manufacturing an anode composition for use in a sealed rechargeable cell.

BACKGROUND OF THE INVENTION

Rechargeable galvanic cells comprise a cathode, a zinc anode, a separator having at least one layer of a semi permeable membrane and an aqueous alkaline electrolyte, such as an aqueous solution of potassium hydroxide. The cathode may comprise manganese dioxide, hydrogen recombination catalysts, hydrogen absorbers, or an air electrode. Graphite and/or carbon black is admixed to the cathode materials to provide electronic conductivity and alkaline electrolyte is admixed to provide ionic conductivity. The zinc anode mixture will include zinc or a zinc alloy as one of the main constituents, and will also include electrolyte and other constituents in known manner. These cells display superior electrical performance, in particular at high discharge rates and at low temperatures, and are widely used in many applications.

In contrast to rechargeable galvanic cells, primary galvanic cells are only discharged once and then discarded. Therefore, the performance requirements or expectations of primary and rechargeable cells are fundamentally distinct. Primary cells are expected to exhibit low self-discharge rates and satisfy demanding performance requirements. Rechargeable cells, on the other hand, are expected to demonstrate good cycle life and cumulative performance. Both types are expected to show low rates of gassing, however, the mechanisms affecting gassing are very different in rechargeable cells as gassing is measured over many recharge cycles, which alters the states of the electrodes many times. The recharge process of zinc electrodes is particularly troublesome due to zinc redistribution and the high solubility of the zinc electrode discharge product in strong alkaline electrolytes. These factors contribute to or cause observed shape changes, poorer cycle life, gassing and formation of dendrites. As a result, it has been very difficult to produce sealed rechargeable cells with zinc electrodes without providing a resealable venting mechanism that would release excessive gassing during cycling and storage. It would be, therefore, not feasible to attempt to predict the effect of a change in, for example, electrode

1 make-up, on the performance of a rechargeable cell from the effect of such a change on the
2 performance of primary cells.

3 Because of environmental concerns regarding disposal of batteries, toxic additives in
4 manganese/zinc cells such as mercury and lead are being drastically reduced or eliminated from
5 the cells. U.S. Patent No. 5,626,988 describes in its background how the addition of mercury
6 provides inhibition of zinc corrosion, resultant hydrogen gassing and electrolyte leakage. It also
7 describes how mercury provides conductivity in the anode resulting in superior electrical
8 performance, in particular at high discharge rates, at low temperature and under conditions where
9 the cells are exposed to mechanical shock and vibration. It further describes the use of
10 surfactants and various metals including indium, for inhibiting corrosion and preventing dendrite
11 formation in rechargeable cells.

12 Also described is known art relating to primary or single use galvanic cells regarding the
13 problem of the surface coating of zinc powders with appropriate metals or their compounds,
14 prior to processing the negative electrode, many of the techniques being complicated and
15 frequently requiring washing and drying steps.

16 U.S. Patent No. 5,626,988 further describes a sealed rechargeable cell containing a
17 mercury-free zinc anode and a method of manufacture, which includes treating a zinc or zinc
18 alloy powder with indium sulfate, and more particularly with both an organic surfactant and
19 electrolyte. The zinc powder is coated with a surfactant, and separately with an acidic aqueous
20 solution of indium sulfate. Without any subsequent filtering, washing or drying, the powder is
21 mixed with electrolyte and gelling agent and assembled into the cell.

22 23 **SUMMARY OF THE INVENTION** 24

25 In one broad aspect of this invention is a method of manufacturing an anode composition
26 for use in a rechargeable electrochemical cell, wherein the anode comprises an electrochemically
27 active material, the method comprising the steps of:

- 28 (a) mixing said material with a first portion of an alkaline electrolyte solution;
- 29 (b) mixing said material with an organic surfactant;
- 30 (c) mixing said material with a first indium compound;
- 31 (d) mixing to said material a second portion of said electrolyte and a gelling agent.

1
2 In another broad aspect of this invention is a method of manufacturing an anode
3 composition for use in a rechargeable electrochemical cell, wherein the anode comprises an
4 electrochemically active material, the method comprising the steps of:

- 5 (a) mixing said material with an organic surfactant;
6 (b) mixing said material with a first indium compound;
7 (c) mixing said material with a first portion of an alkaline electrolyte solution;
8 (d) mixing said material with a second indium compound; and
9 (e) mixing to said material a second portion of said electrolyte and a gelling agent.
10

11 This invention also contemplates a rechargeable cell comprising an anode having the
12 composition manufactured in accordance with the method described herein; a cathode, an
13 electrolyte; and a separator between the anode and the cathode.
14

15 **BRIEF DESCRIPTION OF THE DRAWINGS**

16

17 FIG. 1 is a cross-sectional elevation of a typical cylindrical cell as known in the prior art.

18 FIG. 2 is an enlarged cross-sectional view of the bottom portion of the cell as shown in
19 Fig.2 of earlier U.S. Pat. No. 6,099,987.
20

21 **DESCRIPTION OF THE PREFERRED EMBODIMENTS**

22

23 As shown in Figure 1, a typical alkaline manganese dioxide-zinc rechargeable cell
24 comprises the following main units: a steel can 12, optionally coated with a conductive coating
25 on the inside of the can, defining a cylindrical inner space, a manganese dioxide cathode 14
26 formed by a plurality of hollow cylindrical pellets 16 pressed in the can, a zinc anode 18 made of
27 an anode gel and arranged in the hollow interior of the cathode 14, and a cylindrical separator 20
28 separating the anode 18 from the cathode 14. The ionic conductivity between the anode and the
29 cathode is provided by the presence of potassium hydroxide, KOH, electrolyte added into the cell
30 in a predetermined quantity.

31 The can 12 is closed at the bottom, and it has a central circular pip 22 serving as the
32 positive terminal. The upper end of the can 12 is hermetically sealed by a cell closure assembly

1 which comprises a negative cap 24 formed by a thin metal sheet, a current collector nail 26
2 attached to the negative cap 24 and penetrating deeply into the anode gel to provide electrical
3 contact with the anode, and a plastic top 28 electrically insulating the negative cap 24 from the
4 can 12 and separating gas spaces formed beyond the cathode and anode structures, respectively.

5 The material of separator 20 consists of two different materials, i.e.: a first material made
6 of fibrous sheet material wettable by the electrolyte, and a second material being impermeable to
7 small particles but retaining ionic permeability. An expedient material for the first layer is a
8 sheet material of non-woven polyamide fiber, which is absorbent and serves as a reservoir for
9 electrolyte. The macro-porous structure of the absorbent layer cannot prevent internal shorting
10 by zinc dendrites or deposits during discharge/charge cycling.

11 Shorting is prevented by the second material, which may be a layer or layers of micro-
12 porous or non-porous material laminated to or coated onto the fibrous sheet material. One
13 suitable material is one or more cellophane membranes laminated to the non-woven polyamide
14 sheet. Another is one or more coatings of regenerated cellulose or viscose coated onto and
15 partially impregnating the non-woven polyamide sheet, resulting in a composite material.

16 One or more layers of the laminated or composite material are wound to form a
17 cylindrical tube and placed into the hollow cylindrical cathode structure.

18 As illustrated in Figure 1, one prior art method of achieving sealing of the separator
19 bottom is by means of a hot-melt bead 34, which was used to seal the separator 20 to a washer 33
20 in the cell. In another variation the washer is omitted and hotmelt adhesive only is used.

21 Figure 2 illustrates a bottom sealing means according to an earlier invention described in
22 U.S. Pat. No. 6,099,987. As shown, the sealing of the bottom of the separator 20 is achieved in
23 that invention by two cups 35 and 36, placed around and inside the bottom of the separator. As
24 mentioned above, the separator 20 is preferably comprised of two layers, shown as 20a and 20b.
25 The cup or cups, 35 and 36, are made of a material comprising one or more thin micro-porous or
26 non-porous membranes laminated or coated onto one or more sheets of non-woven fibrous
27 porous sheet material. During placement, the non-woven fibrous materials of the separator and
28 the cup or cups are compressed in the overlap area 34 where the cup and/or cups overlap the
29 bottom of the separator 20. Any gaps between the separator and cup or cups formed by the
30 wrinkling of the thin micro-porous or non-porous layers are filled by the compressed fibers of
31 the porous non-woven layers resulting in an effective barrier to internal short circuits. This is

1 accomplished by selection of the material in the cups and the shape and dimensions of the tools
2 used to make the placement of the cups and the separator into the hollow cathode cylinder.

3 In accordance with the present invention, the anode comprises of zinc as the
4 electrochemically active material. The zinc may be a mercury-free or mercury-free and lead-free
5 zinc or zinc alloy. The mercury-free or mercury-free and lead-free zinc or zinc-alloy may be
6 metallic, a powder, granular, particulate, or in the form of flakes but are not limited to these
7 forms. The metallic zinc powder preferably has a purity of 99.98%, while the zinc alloy powder
8 preferably comprises 99% zinc. Up to about 20% by weight of solid zinc oxide may be
9 incorporated into the active material of the anode. The zinc alloy may comprise of mercury-free
10 and lead-free zinc-bismuth alloy, mercury-free and lead-free zinc-bismuth alloy of finer particle
11 size, zinc-lead alloy, zinc-aluminum-bismuth-indium alloy, zinc-calcium-bismuth-indium alloy,
12 zinc-magnesium-bismuth alloy, and any combination thereof. The zinc may contain up to 800
13 ppm lead, up to 800 ppm indium, up to 500 ppm calcium, up to 500 ppm magnesium, up to 200
14 ppm bismuth and up to 200 ppm aluminum.

15 In a first broad aspect of the invention, the electrochemically active material comprises a
16 mercury-free or mercury-free and lead-free zinc or zinc alloy, which is first mixed with a first
17 portion of an alkaline electrolyte. The electrolyte is preferably potassium hydroxide, the first
18 portion of which is usually added to about 40% of the total electrolyte volume. This ratio is,
19 however, not critical as a 100% of the electrolyte can be applied in the first step, providing the
20 blending system or equipment can produce a lump free pumpable anode gel. It has been
21 determined however, that a preferable range for the first portion of the electrolyte is between
22 about 20% to about 60% of the total volume of electrolyte with about 40% being the most
23 preferable. The zinc is then mixed with an organic surfactant or wetting agent. A wetting agent
24 or surfactant is effective in minute concentrations and should be stable in the alkaline electrolyte.
25 The preferred surfactants for rechargeable cells are selected from the group of nonionic and ionic
26 surfactants having a molecular weight of from about 300 to about 1500, and more particularly
27 are compounds containing polyethylene oxide or polypropylene oxide groups, their copolymers
28 or any combination thereof. Particularly suitable surfactants include polyoxypropylene
29 compounds, polyoxythelene compounds, their copolymers or any combination thereof. The
30 materials are thoroughly mixed to assure complete mixing of the zinc if surfactant is added at
31 this stage. The zinc is then thoroughly mixed with a first indium compound. The indium

1 compound is preferably indium sulfate either in the form of a solution or powder. The indium
2 compound can also be indium oxide, indium hydroxide or indium acetate. The indium
3 compounds used can be either in the form of a solution or a powder. This step is then followed
4 by the addition and thorough mixing of the remainder of the alkaline electrolyte and a gelling
5 agent. This last step can include the addition of nucleation additives such as magnesium oxide,
6 magnesium hydroxide, calcium oxide, calcium hydroxide, zirconium oxide and any combination
7 thereof. The nucleation additives can also be added directly to the electrochemically active
8 material before any of the steps described herein.

9 Nucleation additives function as precipitation aids for zinc oxide during discharge and
10 zinc during the charging process. This results in a better morphology of the rechargeable zinc
11 anode, which can improve performance and lower gassing.

12 The steps described above need not be carried out strictly in the sequential order
13 described above. Some of the steps can be carried out simultaneously with the proviso that the
14 indium compounds are added in an alkaline environment and lead to an anode composition
15 which provides for a better performance rechargeable cell.

16 Thus, in another aspect, the addition of the organic surfactant can precede the addition of
17 the first portion of the alkaline electrolyte.

18 In another aspect, the addition of organic surfactant can precede the addition of the first
19 portion of the alkaline electrolyte and the addition of the first indium compound is then followed
20 by the addition of a second indium compound. If the first indium compound is indium sulfate,
21 the second indium compound can be indium sulfate, indium oxide, indium hydroxide, or indium
22 acetate. The first and second indium compound can be in the form of a solution or in the form of
23 a powder or a combination thereof.

24 In another aspect, the organic surfactant and the first indium compound can be added
25 simultaneously.

26 In another aspect, the addition of the organic surfactant can precede the addition of the
27 first portion of the alkaline electrolyte and the addition of the alkaline electrolyte and first indium
28 compound can be added simultaneously.

29 In another aspect, the addition of the first and second indium compound can be
30 performed simultaneously. Alternatively, the first and second indium compounds can be added
31 simultaneously with the organic surfactant.

1 In a second broad aspect of the invention, the electrochemically active material comprises
2 a mercury-free or mercury-free and lead-free zinc or zinc alloy, which is first mixed with an
3 organic surfactant or wetting agent. The preferred surfactants for rechargeable cells are selected
4 from the group of nonionic and ionic surfactants having a molecular weight of from about 300 to
5 about 1500, and more particularly are compounds containing polyethylene oxide or
6 polypropylene oxide groups, their copolymers or any combination thereof. Particularly suitable
7 surfactants include polyoxypropylene compounds, polyoxythelene compounds, their copolymers
8 or any combination thereof. This step is followed by the addition of a first indium compound.
9 The first indium compound may comprise indium sulfate, indium oxide, indium hydroxide or
10 indium acetate and can be either in the form of a solution or a powder. The electrochemically
11 active material is next mixed with a first portion of an alkaline electrolyte solution. The alkaline
12 electrolyte solution is preferably potassium hydroxide and is preferably added in an amount of
13 about 40% of the total volume of the electrolyte to be added. This ratio is, however, not critical
14 as a 100% of the electrolyte can be applied in the first step, providing the blending system or
15 equipment can produce a lump free pumpable anode gel. It has been determined however, that a
16 preferable range for the first portion of the electrolyte is between about 20% to about 60% of the
17 total volume of electrolyte. A second indium compound is next added to the composition. The
18 second indium compound may be either indium sulfate, indium oxide, indium hydroxide, or
19 indium acetate and can be either in the form of a solution or a powder. Finally, this step is
20 followed by the addition of the remainder of the alkaline electrolyte and a gelling agent. This last
21 step can include the addition of nucleation additives such as magnesium oxide, magnesium
22 hydroxide, calcium oxide, calcium hydroxide, zirconium oxide and any combination thereof.
23 The nucleation additives can also be added directly to the electrochemically active material
24 before any of the steps described herein. In all of the steps the electrochemically active material
25 is thoroughly mixed to ensure complete and homogenous mixing of each component added.

26 The steps described need not be carried out strictly in the sequential order described
27 above. Some of the steps, for example, can be carried out simultaneously with the proviso that
28 anode composition results in rechargeable cell which provide better performance. For example,
29 in one embodiment, the addition of the first indium compound can be added simultaneously with
30 the organic surfactant.

1 The anode composition prepared by the embodiments described herein need no further
2 treatment such as washing and drying before being assembled into the cells.

3 A gelled zinc anode manufactured by the method described herein can be used in
4 rechargeable alkaline manganese dioxide/zinc galvanic cells. These cells can be assembled in
5 cylindrical, button, coin or prismatic formats. Zinc anodes manufactured by the method of the
6 present invention typically contain 1.43 to 2.4 grams of zinc powder per cm^3 of gel.

7 In the case of rechargeable cells using pasted or flat electrodes, depending on whether the
8 cell is assembled in the charged or discharged state, there can be a ratio of zinc to zinc oxide of
9 from 10/90 (discharged state) to 100/0 (fully charged state). The aqueous electrolyte is usually
10 25% to 40% potassium hydroxide, optionally with zinc oxide dissolved in it up to saturation. The
11 negative electrode is processed by kneading the zinc/zinc oxide powder mixture with 4% to 10%
12 colloidal PTFE suspension by weight of zinc, and the paste is subsequently applied to at least
13 one side of a current collector by e.g. a rolling process followed by an optional pressing step.

14 A variety of cathode materials can be used with the anode 18 of the present invention.
15 The cathode active materials may comprise one of manganese dioxide, manganese
16 oxyhydroxide, bismuth modified manganese dioxide, silver oxide, nickel oxyhydroxide or
17 oxygen in an air electrode. Electrolytic manganese dioxide is suitable for use in the positive
18 electrode with the zinc electrode of the present invention. Also included with the manganese
19 dioxide is: 4% to 15% by weight of graphite and carbon black to provide conductivity; minor
20 amounts below 1% by weight of a hydrophobic lubricant such as polytetrafluoroethylene,
21 polyethylene or a metal stearate to provide lubricity during processing and facilitate gas
22 penetration into the electrode; the addition of compounds such as barium oxide, hydroxide or
23 sulfate, in the range of 3 to 15% by weight to improve performance during discharge/discharge
24 cycling; and 0.01% to 10% finely divided hydrogen recombination catalyst such as silver or its
25 oxides or hydrogen absorbing alloys such as LaNi_x or NiTi_y , to prevent pressure build-up from
26 gassing resulting from corrosion of the zinc: and enough 20% to 40% potassium hydroxide
27 electrolyte solution to substantially fill the pores of the manganese dioxide and the pores between
28 the solid powders of the cathode.

29 Various examples will now be described. The cells are AA size or IEC LR6, but
30 rechargeable. These have been subjected to various tests as identified, but in all cases the default
31 charge condition is 12 hours voltage-limited taper charge to an end voltage of 1.65 volts.

1 In each trial four cells were tested on each test. Some anode designs were evaluated in
2 several trials as noted in the tables.

3 The subject of this disclosure is the anode preparation process. The critical requirements
4 to evaluate the designs are electrical cycling performance and gassing. In the rechargeable
5 alkaline manganese zinc cell design, performance is measured using similar discharge loads and
6 voltage endpoints as primary alkaline manganese zinc cells.

7 In performance test 1, cells are deep-discharged through a 3.9-Ohm resistor load to
8 0.80V, then recharged as described above and further discharged and recharged for a total of 25
9 cycles. This test represents motor/toy applications. Performance in Ah-capacity is reported for
10 the first discharge cycle and cumulative performance in Ah is reported over the 25 cycles.

11 Performance test 2 is similar to performance test 1, except that the discharge is through a
12 2.2-Ohm resistor load to 0.8V, representing higher rate applications.

13 Gassing of rechargeable alkaline manganese zinc cells is necessarily higher than that of
14 primary cells as a result of the recharging and longer service life. It is desirable to keep internal
15 cell pressure below 350 psi, which in the AA size cell design represents below about 9 ml of in-
16 cell gas in order to avoid leakage and provide a suitable factor of safety with respect to cell
17 hardware and the safety vent which is not resealable. The following two tests have been found to
18 be severe and are practical for predicting suitability for consumer use.

19 In gassing test 1, fresh cells are stored for 2 weeks at 65C, then deep discharged through
20 2.2 Ohms to 0.80V and recharged for a total of 5 cycles, then stored for approximately one
21 month at room temperature. The cells are then punctured, the gas collected, measured and
22 reported in ml.

23 In gassing test 2, cycled cells are stored at high temperature. Cells are first deep
24 discharged through 2.2 or 3.9 Ohms to 0.80V and recharged for a total of 5 cycles, then stored
25 for 1 week at 65C, then deep discharged and recharged for 5 more cycles, then stored for
26 approximately one month at room temperature. The cells are then punctured, the gas collected,
27 measured and reported in ml.

28 In the examples given the design of the can, cathode, separator and electrolyte remains
29 the same and only the anode design and process of preparation is changed.

Example 1

The zinc used in anode designs A through H is a powder of lead-free zinc containing 133 ppm bismuth, with particle size distribution 19% +60 mesh, 30% -60 +100 mesh, 21% -100 +140 mesh, 20% -140 +200 mesh, 9% -200 +325 mesh and 0.4% -325 mesh. Test results appear in table 1.

In design A the anode is prepared according to the prior art method described in U.S. Patent No. 5,626,988. The zinc in the amount of 65% by weight of the anode is mixed with an aqueous solution of polyethylene glycol surfactant of molecular weight 600 in the amount of 0.05% by weight of surfactant to the weight of the gelled anode. The zinc is then mixed with an aqueous solution of indium sulfate in the amount of 0.1% indium by weight to the weight of zinc in the anode. A portion of the electrolyte is then added and mixed. Carbopol gelling agent is then added in the amount 0.054% by weight to the weight of the anode and mixed. The remaining electrolyte is then added in an amount to provide a total weight of electrolyte of 33% by weight to the weight of the anode. The performance and gassing results of the other designs in example 1 are compared to the results of this control design and process.

In design B the anode constituents are the same as in design A. However, in anode design B, the order in which the constituents are mixed differ from that in anode design A. In design B, a first portion of the electrolyte is added and mixed first followed by the surfactant and then the indium sulfate solution. A second portion of the electrolyte is next mixed together with the gelling agent. The first portion is typically chosen at the 40% level of the total of first and second portion of electrolyte. This ratio is not critical for the purpose of this invention, as all the electrolyte could be applied as the first portion (100%), provided the blending system or equipment can produce a lump free pumpable anode gel. However, it was determined that a preferable range for first electrolyte is between 20 and 60%, most preferably 40%, which was used for the examples of this application. The performance of this design is 1 to 9% higher than design A and the gassing is similar or less. The alkaline plating process created by adding electrolyte before the surfactant and indium sulfate solution provides benefits.

In design C the anode constituents are the same as in design B, but the surfactant is mixed with the zinc before the addition of any electrolyte and the indium sulfate solution is added after addition of the first portion of electrolyte. The addition of indium sulphate is followed by the addition of a second portion of the electrolyte and the gelling agent. The performance of this

1 design is on average lower than designs A and B, and gassing is somewhat higher as well, but
2 still within an acceptable level of gas as required by the cell hardware. There does not appear to
3 be any benefit in mixing the zinc with surfactant before the addition of electrolyte.

4 Design D is similar to design B except that solid indium oxide powder is used in place of
5 indium sulfate solution in an amount to provide 0.1% indium by weight to the weight of zinc in
6 the anode. Performance of this design is 6 to 13% higher than control group A and better than
7 group B as well. However, this benefit is offset by gassing that is up to four times that of designs
8 A and B, but is still within the acceptable level of gas determined by the cell hardware.

9 Design E is similar to design D except that the amount of indium oxide used provided
10 0.2% indium by weight to the weight of zinc in the anode, double that of design B. Performance
11 of this design is on average about the same as design D and gassing is lower than design D but
12 still higher than designs A and B. In primary alkaline cells, amounts of indium of 0.10% to zinc
13 or higher are typically avoided as a gassing inhibitor because of undesirable effects on
14 performance, but in this rechargeable alkaline cell design there is a demonstrated benefit in the
15 higher levels of indium, both for gassing and performance.

16 In design F, the anode constituents are the same as in design D, but the surfactant is
17 mixed with the zinc before the addition of any electrolyte and the indium oxide powder is mixed
18 in after the addition of the first portion of electrolyte. A second portion of the electrolyte is then
19 mixed together with the gelling agent. In this design, performance is much better than design A
20 but there is no benefit to performance versus design D and gassing is slightly higher. Of these
21 two process designs, mixing in the surfactant and indium oxide after the electrolyte is better.

22 Design G is similar to design B and D except that 0.02% of the total indium is mixed in
23 as indium sulfate solution after the first portion of electrolyte, and 0.08% of the total indium is
24 mixed in as indium oxide powder after the addition of the indium sulfate solution. Performance
25 is much higher than design A, and similar to design D. Gassing is higher than design A and
26 similar to design D. The use of indium sulfate solution to provide 0.02% of the indium does not
27 seem to have the desired effect of moderating the gassing.

28 Design H is similar to design G except that 0.05% of the total indium is mixed in as
29 indium sulfate solution and 0.05% of the total indium as indium oxide powder. Performance is 1
30 to 6% higher than design A, but up to 6% lower than design D. Gassing is up to 3 times higher
31 than design A and about two thirds of design D. The use of indium sulfate solution to provide

1 one-half of the indium does have the desired effect of moderating the gassing, offset by a slight
2 decrease in performance.

3 This example demonstrates the principle that rechargeable performance can be increased
4 and gassing controlled by means of anode designs and processes where the organic surfactant
5 and indium compound inhibitors is added after the zinc is mixed with electrolyte, or partly before
6 and partly after the zinc powder is mixed with electrolyte. It also demonstrates that the choice of
7 indium compound and when it is added during the process is important with respect to
8 performance enhancement and the management of gassing.

9 Example 2

10 The zinc powder used in anode designs J through P is lead-free zinc containing 133 ppm
11 bismuth as in example 1, but of a much finer particle size. The particle size distribution is 10%
12 +60 mesh, 19% -60 +100 mesh, 18% -100 +140 mesh, 18% -140 +200 mesh, 16% -200 +325
13 mesh and 19% -325 mesh. Test results appear in table 2.

14 Anode design J is prepared in the same manner as design A of example 1 and serves as
15 the prior art control design to which the other designs of this example are compared. It gives
16 higher first discharge performance than design A, but similar or lower cumulative performance
17 over 25 cycles. Gassing is a little higher than design A, but at a low level.

18 In design K, the surfactant and indium sulfate are mixed in after a portion of the
19 electrolyte as in design B after which a second portion of the electrolyte together with the gelling
20 agent is added and mixed. The alkaline plating process created by adding electrolyte before the
21 surfactant and indium sulfate solution provide little performance benefit in this case but some
22 benefit in reduced gassing.

23 Design L is prepared as in design D with surfactant and indium oxide powder added after
24 electrolyte. Similar to the results in design D, cumulative performance is greatly enhanced, in
25 this case by 13% on test 1 and 7% on test 2. Gassing is 1.5 to 2 times that of design J, but this
26 increase is less than that of design D versus design A.

27 Design M is prepared in a similar way to design L, except that indium hydroxide powder
28 is used in place of indium oxide powder. Compared to control design J, performance is similar or
29 lower and gassing is similar or a little higher. Compared to design L with indium oxide,
30 performance is lower and gassing the same or lower. There seemed to be no advantage to mixing
31 indium hydroxide with the zinc of this example.

1 In design N the surfactant is mixed with the zinc. Then, 0.02% of indium to zinc is mixed
2 into the zinc as indium sulfate solution. The zinc is then mixed with a first portion of the
3 electrolyte. 0.08% of indium to zinc is next added and mixed in as indium sulfate solution
4 followed by the remainder of the electrolyte and together with the gelling agent. Compared to
5 design J where the surfactant and all of the indium sulfate is added before any electrolyte,
6 performance is a little higher and gassing is a little lower. Compared to design K, where the
7 surfactant and all of the indium sulfate solution is added after a portion of the electrolyte,
8 performance and gassing are similar.

9 Design P is prepared similarly to design N, except that 0.05% indium to zinc is added and
10 mixed as indium sulfate solution before any electrolyte and 0.05% indium to zinc is added and
11 mixed as indium sulfate solution after a first portion of the electrolyte. Performance is similar to
12 that of the control design J and gassing is somewhat lower. Compared to design K, performance
13 and gassing are similar.

14 This example demonstrates the performance improvement achieved by mixing the indium
15 compound, particularly indium sulfate after mixing in the zinc with a first portion of the
16 electrolyte. It further demonstrates the possibility of reducing gassing by mixing a first portion of
17 indium sulfate solution before any electrolyte and the second remaining portion of indium sulfate
18 solution after mixing a first portion of the electrolyte.

19 **Example 3**

20 The zinc powder used in anode designs Q through V is zinc containing 400-550 ppm
21 lead. The particle size distribution is 22% +60 mesh, 34% -60 +100 mesh, 22% -100+140 mesh,
22 16% -140 +200 mesh, 6% -200 +325 mesh. Test results appear in table 3.

23 Anode design Q is prepared in the same manner as design A of example 1 and serves as
24 the prior art control design to which the other designs of this example are compared. It gives
25 higher first discharge performance than design A, but lower cumulative performance over 25
26 cycles. Gassing is at a low level.

27 In design R, the surfactant and indium sulfate are added and mixed after a first portion of
28 the electrolyte as in design B. This is then followed by the addition and mixing of a second
29 portion of the electrolyte and a gelling agent. The alkaline plating process created by the mixing
30 in of the first portion of the electrolyte before the surfactant and indium sulfate solution provide

1 10% and 3% benefits in cumulative performance. Gassing is increased up to double the low
2 levels of the control design Q.

3 Design S is prepared as in design D with surfactant and indium oxide powder added and
4 mixed after a first portion of the electrolyte. This is then followed by the mixing and addition of
5 a second portion of the electrolyte and a gelling agent. Similar to the results in design D,
6 cumulative performance is greatly enhanced, in this case by 8% on test 1 and 16% on test 2.
7 Gassing is lower on test 1 but 3 times that of design Q on test 2.

8 Design T is prepared in a similar way to design M, using indium hydroxide powder in
9 place of indium oxide powder. Compared to the control design Q, both first discharge and
10 cumulative performance are higher and gassing is lower in test 1 and 3 times higher in test 2.
11 Compared to design S with indium oxide, performance is lower and gassing is similar. Contrary
12 to design M of example 2 above, with this zinc there is a performance benefit in using indium
13 hydroxide instead of indium sulfate but not as much benefit as when using indium oxide.

14 In design U, the surfactant is mixed with the zinc powder. 0.02% of indium to zinc is next
15 mixed into the zinc as indium sulfate solution. The zinc is then mixed with a first portion of the
16 electrolyte. 0.08% of indium to zinc is then added and mixed as indium oxide powder followed
17 by a second portion of the electrolyte and the gelling agent. Compared to design Q, where the
18 surfactant and all of the indium as indium sulfate is added before any electrolyte, performance on
19 first discharge is similar and cumulative performance is 18% and 5% higher. However, gassing is
20 about 3 times higher. Compared to design S where the surfactant and all of the indium oxide
21 powder is mixed in after a first portion of the electrolyte, performance is not quite as high, but
22 surprisingly gassing with this zinc is 4 times higher on one test and similar on the other.

23 Design V is prepared similarly to design U, except that 0.05% indium to zinc is added
24 and mixed in as indium sulfate solution before any electrolyte and 0.05% indium to zinc is mixed
25 in as indium oxide powder after a portion of the electrolyte. Cumulative performance is 13%
26 higher on test 1 and similar on test 2 versus that of the control design Q and gassing is 2 to 3
27 times higher. Compared to design S, where the surfactant and all of the indium oxide powder is
28 added and mixed in after a portion of the electrolyte, performance is not quite as high, but
29 surprisingly gassing with this zinc is two and a half times higher on one test and similar on the
30 other.

1 This example, carried out with leaded zinc alloy, further demonstrates the benefit to
2 performance of mixing to this zinc-lead alloy, surfactant and indium compound, particularly
3 indium oxide and, indium hydroxide after mixing the zinc-lead alloy with electrolyte. It further
4 demonstrates that gassing of the zinc can be managed by mixing part of the indium in an acid
5 environment before adding electrolyte and mixing in the remaining indium in an alkaline
6 environment after adding electrolyte.

7 **Example 4**

8 The zinc powder used in anode designs W through Z is zinc alloy containing 104 ppm
9 aluminum, 119 ppm bismuth, 200 ppm indium. The particle size distribution is 20% +60 mesh,
10 35% -60 +100 mesh, 23% -100 +140mesh, 17%-140 +200 mesh, 6% -200 +325. Test results
11 appear in table 4. As the zinc alloy contains 200 ppm indium or 0.02%, the indium added in the
12 anode preparation process is reduced to 0.08% to zinc to provide a total of 0.10% indium to zinc
13 by weight in the anode.

14 Anode design W is prepared in the same manner as design A of example 1 and serves as
15 the prior art control design to which the other designs of this example are compared. It gives
16 similar first discharge performance to design A, but much lower cumulative performance over 25
17 cycles. Gassing is at a low level, somewhat lower than that of design A.

18 In design X, the surfactant and indium sulfate are added and mixed in after a portion of
19 the electrolyte as in design B. The alkaline plating process created by mixing the electrolyte
20 before the surfactant and indium sulfate solution provides a 7% benefit in cumulative
21 performance. Gassing is similar to the low levels of the control design W.

22 In design Y, as in design N, the surfactant is mixed with the zinc powder. 0.016% of
23 indium to zinc is next mixed into the zinc as indium sulfate solution. The zinc is then mixed in
24 with a first portion of the electrolyte. 0.064% of indium to zinc is then mixed in as indium sulfate
25 solution. This step is followed by the addition and mixing of the second portion of the electrolyte
26 and the gelling agent. Compared to design W, where the surfactant and all of the indium sulfate
27 is mixed in before any electrolyte, first discharge performance is 8% and 6% higher and
28 cumulative performance is a little lower on one test and a little higher on the other. Gassing is
29 higher but still at a low level. Compared to design X where the surfactant and all of the indium
30 sulfate solution is mixed in after a portion of the electrolyte, first discharge performance is higher
31 but cumulative performance is lower. Gassing is higher but still at a low level.

1 Similar to design U, in design Z the surfactant is mixed with the zinc. Then 0.016% of
2 indium to zinc is mixed into the zinc as indium sulfate solution. The zinc is then mixed with a
3 first portion of the electrolyte. 0.064% of indium to zinc is next added and mixed in as indium
4 oxide powder. This is then followed by the addition and mixing of the gelling agent and a second
5 portion of the electrolyte. Compared to design W where the surfactant and all of the indium is
6 mixed in as indium sulfate before any electrolyte, first discharge performance is 3% and 9%
7 higher and cumulative performance is 9% and 5% higher. Gassing is 4 times higher on test 1 but
8 at a tolerable level, and lower on test 2. Compared to design Y where indium sulfate solution
9 instead of indium oxide is mixed in after the electrolyte, first discharge performance is lower on
10 one test and similar on the other, but cumulative performance is 11% higher on one test and
11 similar on the other. Gassing is higher on one test, lower on the other, but still at a tolerable
12 level.

13 This example demonstrates that even with zinc containing other metals such as
14 aluminum, bismuth and indium, as corrosion inhibitors and for other purposes, a combination of
15 choice of indium compounds and the order of mixing in the anode composition process can be
16 used to improve cell performance and manage zinc gassing.

17 **Example 5**

18 This example uses the same zinc as in example 1, except that nucleation additives are
19 added during the process as well. The nucleation additives can be added directly to the zinc
20 before the first portion of the electrolyte or with the gelling agent. In this example the nucleation
21 additive was added before the first electrolyte. Test results appear in table 5.

22 Anode design A of example 1 serves as the prior art control in this comparison. Also,
23 design B and D of example 1 are listed for reference. The performance and gassing results of the
24 other designs in example 5 is compared to the results of the control design A.

25 Design BB is similar to design B except that 0.5% magnesium oxide by weight of anode
26 is mixed in as nucleation agent during the anode preparation process. Performance of this design
27 over 25 cycles is similar to 3% better than prior art control design A, but the gassing is only half
28 on gassing test 1 and lower on gassing test 2. Compared to design B, the cumulative performance
29 is about the same, but gassing is lower.

30 Design BC is similar to design B and BB except that a higher amount of 1% magnesium
31 oxide by weight of anode is added and mixed in as nucleation agent during the anode preparation

1 process. Performance of on initial discharge is similar to 9% lower than design A, but over 25
2 cycles cumulative this design showed already a 5 to 6% benefit and the gassing is much lower as
3 well. Compared to design B, the cumulative performance is about the same, but gassing is lower.

4 Design DD is similar to design D except that 0.05% magnesium oxide by weight of
5 anode is mixed in as nucleation agent during the anode preparation process. Performance of this
6 design over 25 cycles is 15 to 23% better than prior art control design A, but the gassing is only
7 half on gassing test 1 and lower on gassing test 2. Compared to design D, performance is 2 to
8 15% better with much reduced gassing.

9 Design BE is similar to design B except that 0.05% calcium oxide by weight of anode is
10 added and mixed in as nucleation agent during the anode preparation process. Performance of
11 this design over 25 cycles is similar to 11% better than prior art control design A and gassing is
12 lower. Compared to design B, performance is similar to 6% better with lower gassing levels.

13 Design DF is similar to design D except that 0.05% calcium oxide by weight of anode is
14 added and mixed in as nucleation agent during the anode preparation process. Performance of
15 this design over 25 cycles is 12 to 15% better than prior art control design A, but gassing is
16 higher than design A. Compared to design D, performance is similar to 5% better with only half
17 the gassing on gassing test 1 and somewhat lower gassing on test 2.

18 Design BG is similar to design B except that 0.05% calcium hydroxide by weight of
19 anode is mixed in as nucleation agent during the anode preparation process. Performance of this
20 design over 25 cycles is 4 to 8% better than prior art control design A and gassing is lower.
21 Compared to design B, performance is 3% better with somewhat lower gassing levels.

22 Design BH is similar to design B and BG except that a higher amount of 0.5% calcium
23 hydroxide by weight of anode is mixed in as nucleation agent during the anode preparation
24 process. Performance of this design over 25 cycles is similar to 11% better than prior art control
25 design A and gassing is lower. Compared to design B, performance is similar to 6% better with
26 lower gassing levels.

27 This example demonstrates that the use of nucleation additives can be advantageously
28 applied in this anode process to improve cell performance and manage zinc gassing.

29 The 5 examples together demonstrate in rechargeable alkaline manganese zinc cells a
30 means of maximizing performance and managing gassing to a tolerable and safe level with zinc
31 powders containing various alloying metals and of various particle size distributions by a choice

1 of indium compounds and the order in which surfactant and indium compounds are mixed in
2 during manufacture of the anode composition, which manufacture requires no subsequent
3 washing, rinsing, drying or other steps before being assembled into cells.

4 The polyethylene glycol surfactant used is soluble in water but insoluble in the
5 concentrated potassium hydroxide electrolyte. Indium sulfate is soluble in water but only slightly
6 soluble in the electrolyte. Indium oxide and hydroxide are even less soluble than indium sulfate.

7 The most efficient and effective method of applying these organic and metallic corrosion
8 inhibitors and mixing the zinc with surfactant and then mixing with indium by cementation is by
9 using aqueous solutions of surfactant and indium sulfate to mix the zinc before mixing of any
10 alkaline electrolyte. Surprisingly, as demonstrated by the examples above, performance can be
11 enhanced and gassing in rechargeable cells can still be managed to a suitable level by mixing
12 part or all of the inhibitors after mixing in of electrolyte.

TABLE 1

Anode Design	No. of trials	Order of addition of Zn, PEG, indium compound and electrolyte (KOH)	Performance Test 1				Performance Test 2				Gassing Test 1	Gassing Test 2
			Cycle 1 Ah	% vs Control 1-	Cycle 25 Cumulative Ah	% vs Control 1	Cycle 1 Ah	% vs Control 1-	Cycle 25 Cumulative Ah	% vs Control 1		
Lead-free zinc-bismuth alloy												
A	9	Zn, PEG, In2(SO4)3, KOH [Prior Art]	1.57		18.97		1.24		15.40		1.8	2.5
B	6	Zn, KOH, PEG, In2(SO4)3	1.58	1%	19.20	1%	1.35	9%	16.23	5%	1.9	2.0
C	1	Zn, PEG, KOH, In2(SO4)3	1.56	-1%	17.63	-7%	1.31	6%	15.14	-2%	3.4	1.9
D	4	Zn, KOH, PEG, In2O3	1.70	8%	21.49	13%	1.31	6%	16.60	8%	7.2	3.7
E	1	Zn, KOH, PEG, In2O3(0.2%In to Zn)	1.61	3%	20.56	8%	1.38	11%	17.56	14%	4.2	3.0
F	1	Zn, PEG, KOH, In2O3	1.56	-1%	20.80	10%	1.34	8%	16.84	9%	7.9	5.5
G	1	Zn, KOH, PEG, In2(SO4)3 (0.02% In to Zn), In2O3 (0.08%In to Zn)	1.59	1%	20.33	7%	1.38	11%	16.78	9%	7.7	3.5
H	1	Zn, KOH, PEG, In2(SO4)3 (0.05% In to Zn), In2O3 (0.05%In to Zn)	1.59	1%	19.26	2%	1.31	6%	16.01	4%	5.2	2.4

TABLE 2

Anode Design	No. of trials	Order of addition of Zn, PEG, indium compound and electrolyte (KOH)	Performance Test 1				Performance Test 2				Gassing Test 1	Gassing Test 2
			Cycle 1 Ah	% vs Control	Cycle 25 ve Ah	% vs Control	Cycle 1 Ah	% vs Control	Cycle 25 Cumulative Ah	% vs Control		
Lead-free zinc-bismuth alloy, finer particle size												
J	2	Zn, PEG, In2(SO4)3, KOH [Prior Art]	1.63		17.38		1.34		15.40		2.3	3.2
K	1	Zn, KOH, PEG, In2(SO4)3	1.63	0%	17.82	3%	1.33	-1%	15.10	-2%	2.6	1.8
L	3	Zn, KOH, PEG, In2O3	1.59	-2%	19.66	13%	1.33	-1%	16.55	7%	4.6	4.8
M	2	Zn, KOH, PEG, In(OH)3	1.54	-6%	16.52	-5%	1.30	-3%	15.63	1%	2.2	4.4
N	1	Zn, PEG, In2(SO4)3 (0.02% In to Zn), KOH, In2(SO4)3 (0.08%In to Zn)	1.70	4%	17.82	3%	1.39	4%	15.03	-2%	2.1	2.0
P	1	Zn, PEG, In2(SO4)3 (0.05% In to Zn), KOH, In2(SO4)3 (0.05%In to Zn)	1.61	-1%	17.87	3%	1.29	-4%	15.02	-2%	2.4	1.8

TABLE 3

Anode Design	No. of trials	Order of addition of Zn, PEG, indium compound and electrolyte (KOH)	Performance Test 1				Performance Test 2				Gassing Test 1	Gassing Test 2
			Cycle 1 Ah	% vs Control 1-	Cycle 25 ve Ah	% vs Control 1	Cycle 1 Ah	% vs Control 1-	Cycle 25 Cumulative Ah	% vs Control 1	Average ml	Average ml
Zinc-lead alloy												
Q	2	Zn, PEG, In2(SO4)3, KOH [Prior Art]	1.60		16.75		1.34		14.94		2.9	1.1
R	1	Zn, KOH, PEG, In2(SO4)3	1.59	-1%	18.44	10%	1.37	2%	15.33	3%	3.6	2.4
S	2	Zn, KOH, PEG, In2O3	1.72	8%	19.41	16%	1.42	6%	17.11	15%	2.1	3.4
T	2	Zn, KOH, PEG, In(OH)3	1.66	4%	17.96	7%	1.37	2%	16.15	8%	1.8	3.7
U	1	Zn, PEG, In2(SO4)3 (0.02% In to Zn), KOH, In2O3 (0.08% In to Zn)	1.61	1%	19.71	18%	1.32	-1%	15.64	5%	7.9	3.6
V	1	Zn, PEG, In2(SO4)3 (0.05% In to Zn), KOH, In2O3 (0.05% In to Zn)	1.58	-1%	19.01	13%	1.27	-5%	15.01	0%	5.2	3.1

TABLE 4

Anode Design	No. of trials	Order of addition of Zn, PEG, indium compound and electrolyte (KOH)	Performance Test 1				Performance Test 2				Gassing Test 1	Gassing Test 2
			Cycle 1 Ah	% vs Control 1-	Cycle 25 Cumulative Ah	% vs Control 1	Cycle 1 Ah	% vs Control 1-	Cycle 25 Cumulative Ah	% vs Control 1		
Zinc-aluminum-bismuth-indium alloy												
W	1	Zn, PEG, In ₂ (SO ₄) ₃ , KOH [Prior Art]	1.50		16.85		1.27		13.61		1.6	1.8
X	1	Zn, KOH, PEG, In ₂ (SO ₄) ₃	1.47	-2%	18.00	7%	1.29	2%	14.52	7%	1.8	1.9
Y	1	Zn, PEG, In ₂ (SO ₄) ₃ (0.016%In to Zn), KOH, In ₂ (SO ₄) ₃ (0.064%In to Zn)	1.62	8%	16.59	-2%	1.34	6%	14.27	5%	2.0	2.9
Z	1	Zn, PEG, In ₂ (SO ₄) ₃ (0.016%In to Zn), KOH, In ₂ O ₃ (0.064%In to Zn)	1.55	3%	18.41	9%	1.34	6%	14.45	6%	4.8	1.1

TABLE 5

Anode Design	No. of trials	Order of addition of Zn, PEG, indium compound and electrolyte (KOH)	Performance Test 1				Performance Test 2				Gassing Test 1	Gassing Test 2
			Cycle 1 Ah	% vs Control 1-	Cycle 25 ve Ah	% vs Control 1	Cycle 1 Ah	% vs Control 1-	Cycle 25 ve Ah	% vs Control 1		
Lead-free zinc-bismuth alloy w/ nucleation agents as anode additive												
A	9	Zn, PEG, In2(SO4)3, KOH [Prior Art]	1.57		18.97		1.24		15.40		1.8	2.5
B	6	Zn, KOH, PEG, In2(SO4)3	1.58	1%	19.20	1%	1.35	9%	16.23	5%	1.9	2.0
D	4	Zn, KOH, PEG, In2O3	1.70	8%	21.49	13%	1.31	6%	16.60	8%	7.2	3.7
BB	1	Zn, KOH, PEG, In(SO4)3, 0.5%MgO	1.58	1%	19.51	3%	1.14	-8%	15.17	-1%	0.7	1.8
BC	2	Zn, KOH, PEG, In(SO4)3, 1%MgO	1.43	-9%	19.89	5%	1.24	0%	16.36	6%	1.1	0.6
DD	1	Zn, KOH, PEG, In2O3, 0.05%MgO	1.51	-4%	21.83	15%	1.36	10%	18.91	23%	0.9	1.6
BE	1	Zn, KOH, PEG, In(SO4)3, 0.05%CaO	1.56	-1%	18.85	-1%	1.37	10%	17.08	11%	1.2	1.4
DF	1	Zn, KOH, PEG, In2O3, 0.05%CaO	1.69	8%	21.16	12%	1.40	13%	17.43	13%	3.3	3.6
BG	1	Zn, KOH, PEG, In(SO4)3, 0.05%Ca(OH)2	1.54	-2%	19.64	4%	1.33	7%	16.59	8%	1.2	2.0
BH	1	Zn, KOH, PEG, In(SO4)3, 0.5%Ca(OH)2	1.62	3%	19.40	2%	1.38	11%	17.12	11%	1.5	1.9